Spacesuits to refrigeration to pipelines: Insulating aerogels

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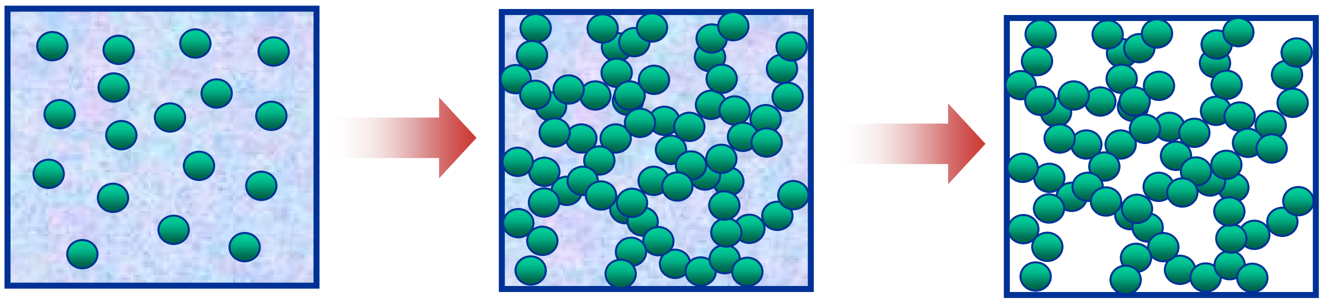
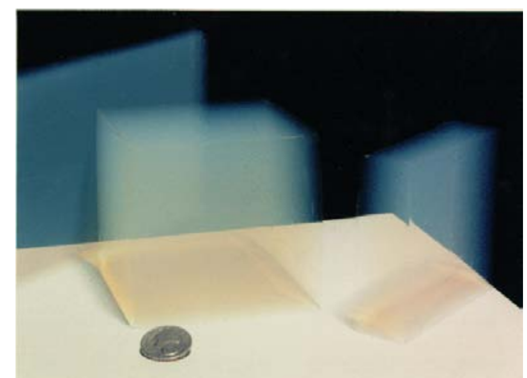
What are aerogels?



Sol Gel Aerogel

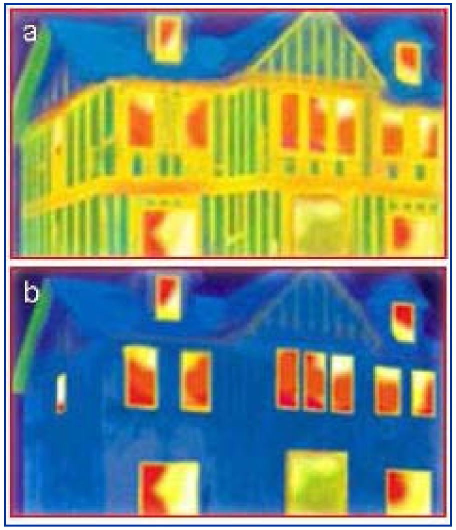
- Highly porous solids made by drying a wet gel without shrinking
- Pore sizes extremely small (typically 10-40 nm)—makes for very good insulation
- 2-4 times better insulator than fiberglass under ambient pressure, 10-15 times better in light vacuum
- Invented in 1930's by Prof. Samuel Kistler of the College of the Pacific



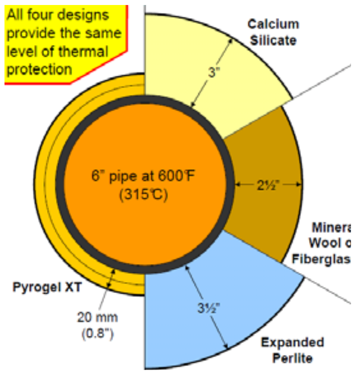
Typical monolithic silica aerogels

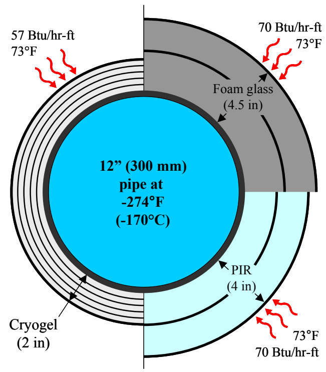
Examples of current commercial aerogel products

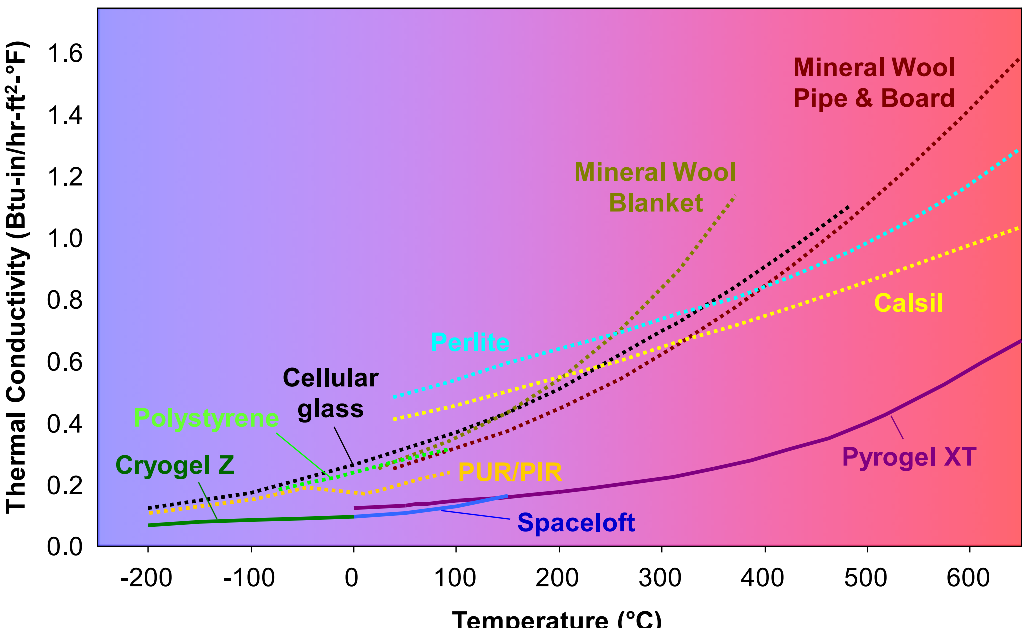
- Cabot
  - Pellets, composite
  - Oil and gas pipeline insulation
  - Cryo-insulation
  - Day-lighting applications
- Aspen Aerogels
  - Flexible blanket insulation
  - Oil and gas pipeline
  - Construction materials
  - Aerospace, apparel
- Nanopore
  - Vacuum insulation panels
  - Shipping containers
  - Refrigeration
  - Apparel



Comparison of Aspen Aerogels blanket insulation with traditional insulation







Example markets

Industrial ($5 billion)

- Lower installed costs through reductions in downtime, labor and logistics costs
- Lower lifecycle costs through reduced on-going maintenance costs

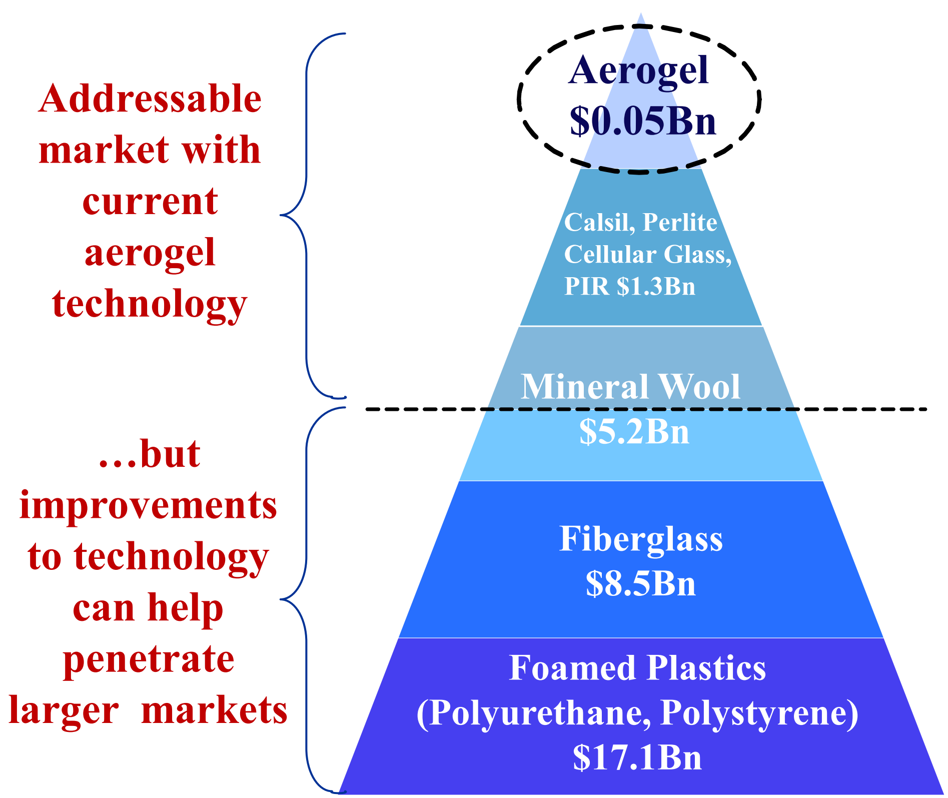
Building and Construction ($23 billion)

- Superior thermal performance and strong fire protection with advantageous form factor
- Enables cost-effective compliance with stringent building regulations, particularly in Europe

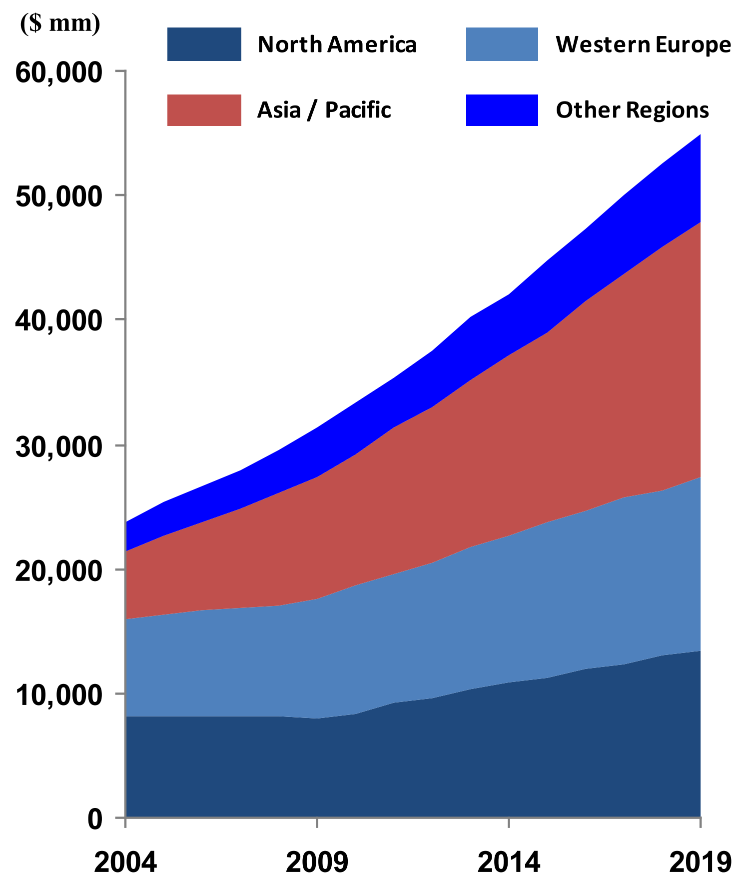
Source: George Gould, Aspen Aerogels

The $32.1 Billion Global Insulation Market

Aerogels Today Only <0.25% Market, but Potential Applications throughout the Global Insulation Market

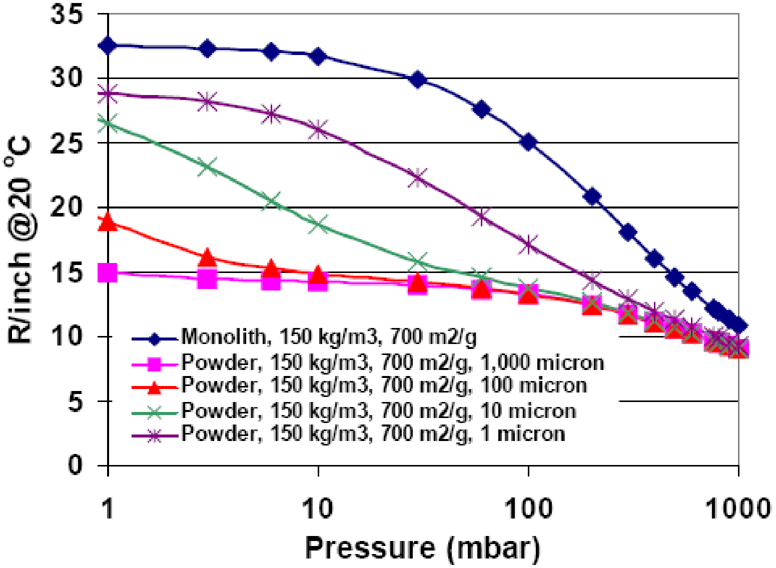


World Insulation Demand (by Region)



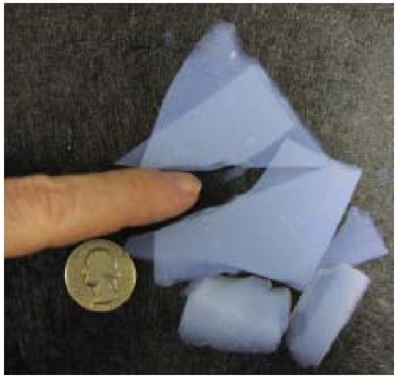
Source: Freedonia Group 2011 World Insulation Report

Monolithic silica aerogels out-perform particulate forms as insulation



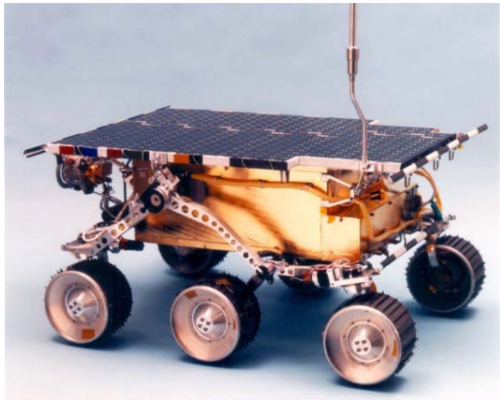
Doug Smith, Aerogel Conference, 2007

but are extremely fragile and moisture sensitive



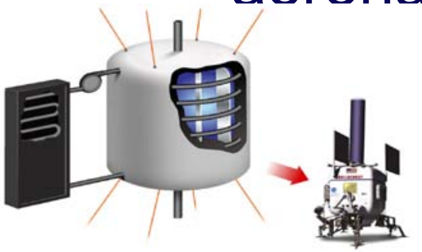
and limited to a few exotic applications

Cosmic dust collector – Stardust Program

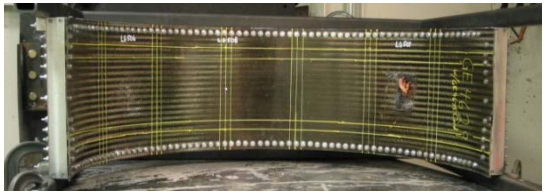


Insulation on rovers

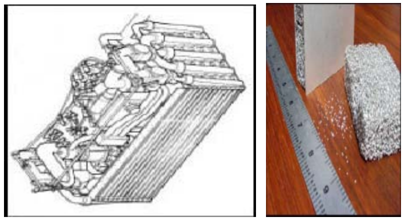
Potential applications for durable aerogels in aeronautics and space exploration



Cryotank Insulation



Fan engine containment (Ballistic protection)

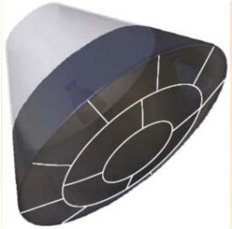


Air revitalization

Ultra-lightweight, multifunctional structures for habitats, rovers

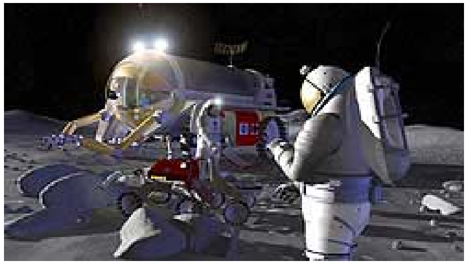
Sandwich structures

Propellant tanks



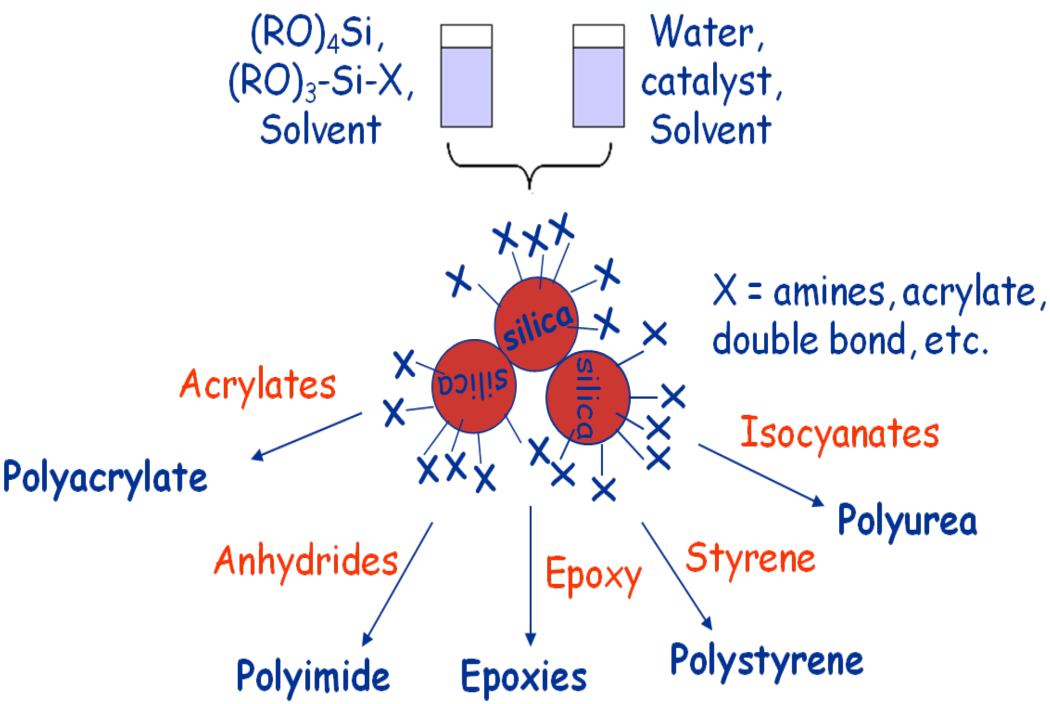
Heat shielding

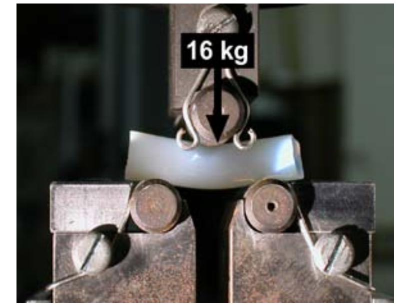
Inflatable aerodynamic decelerators



Insulation for EVA suits and habitats

Durable aerogels by reinforcing with polymers



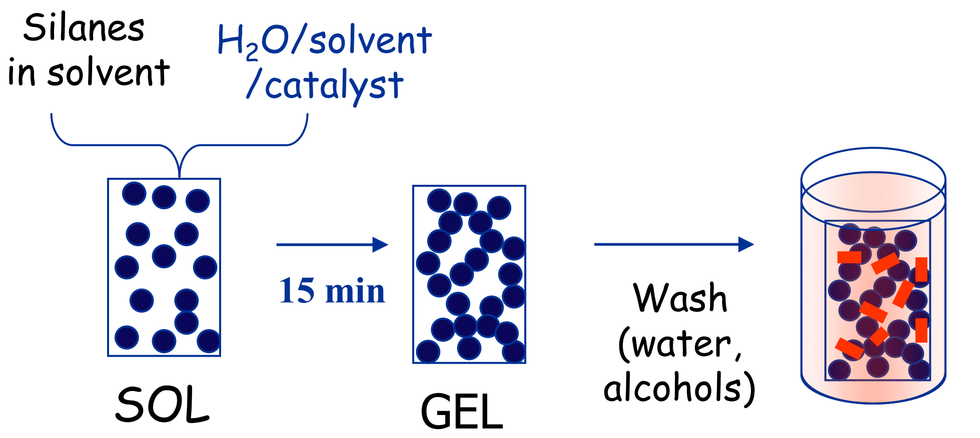


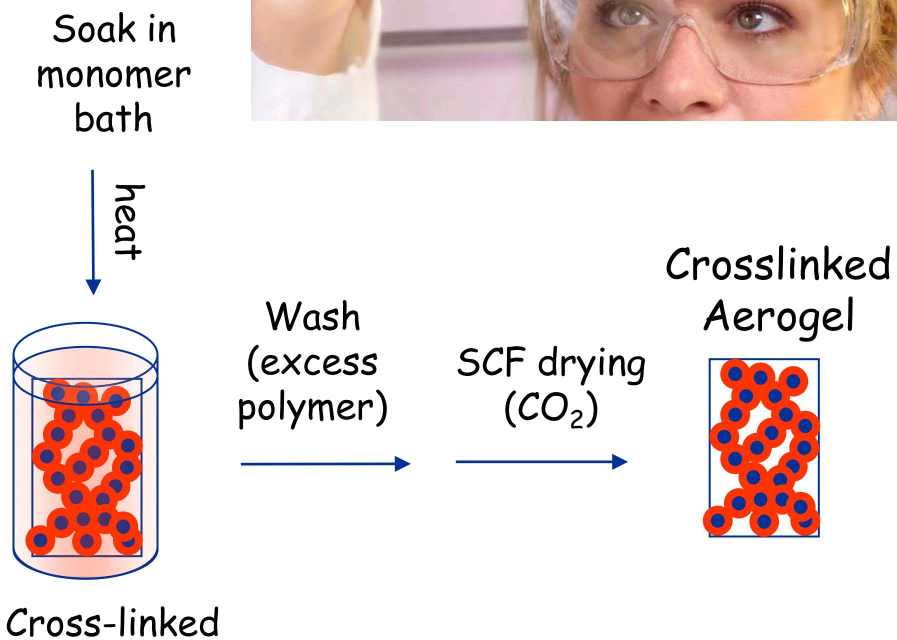
Native Cross-linked

- Polymer reinforcement ***doubles*** the density
- Results in ***two order of magnitude*** increase in strength
- Reduces surface area by only 30-50%

- Leventis, Meador, Johnston, Fabrizio, and Ilhan, US Patent No. 7,732,496; June 8, 2010
- Jason P. Randall, Mary Ann B. Meador, and Sadhan C. Jana, *ACS Appl. Mater. Interfaces*, **2011**, *3* (3), pp 613–626

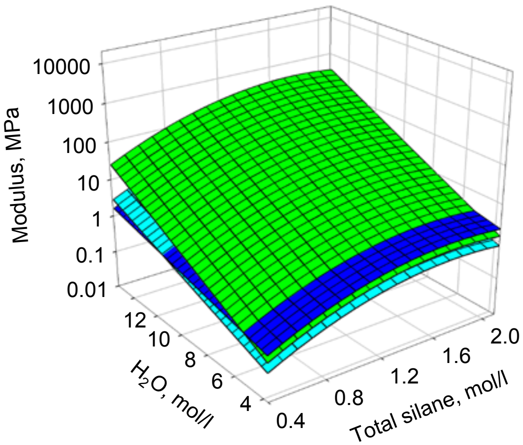
Typical Aerogel Cross-linking Process

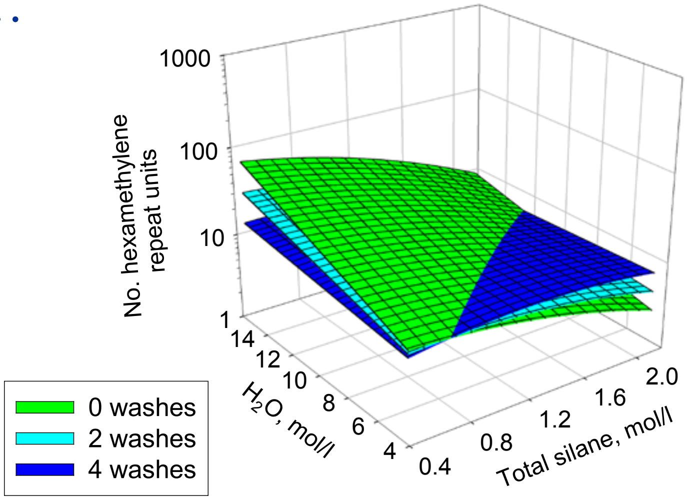




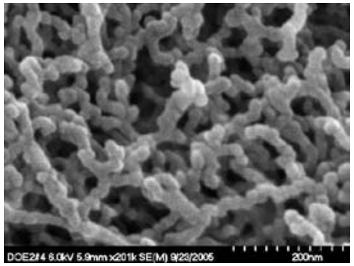
Process/property optimization of di-isocyanate cross-linked aerogels

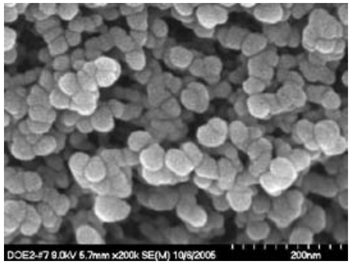
Empirical models…



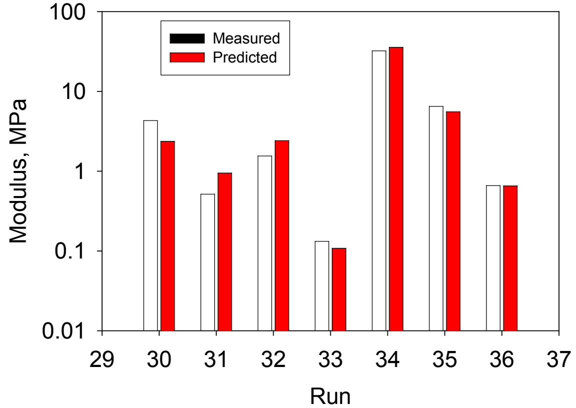


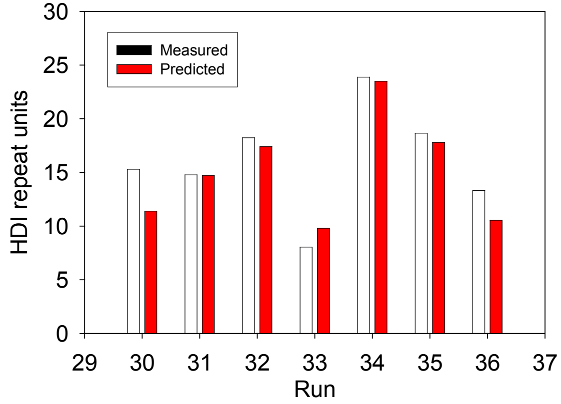
Low density...





…used for predictions of optima

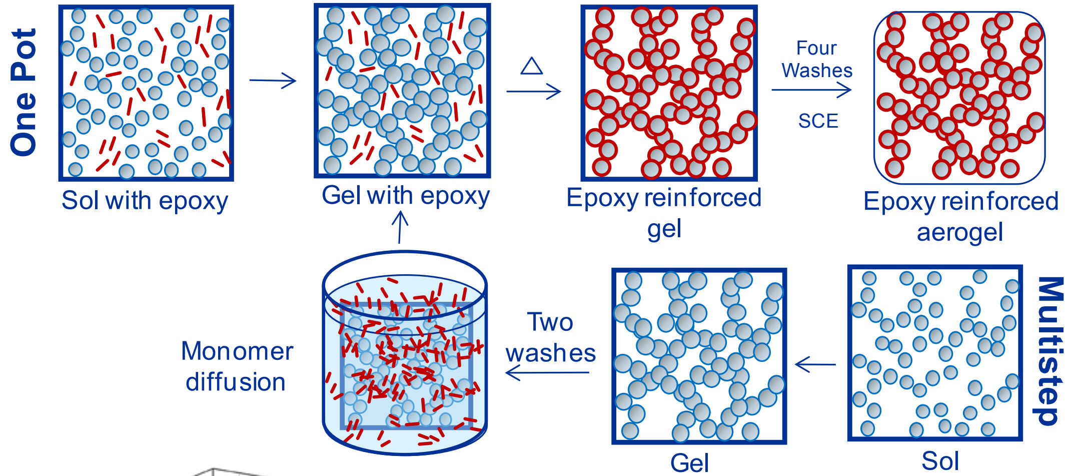


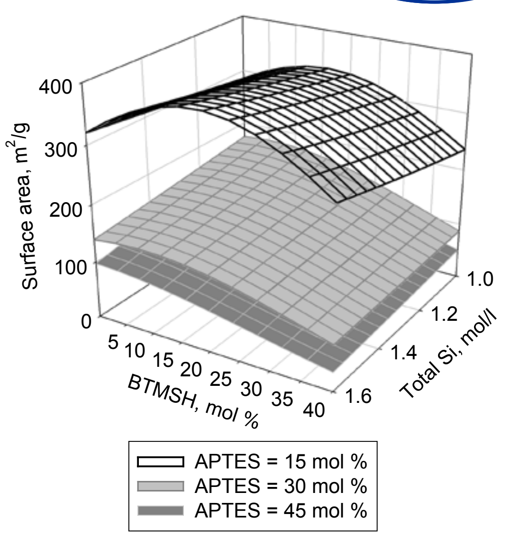


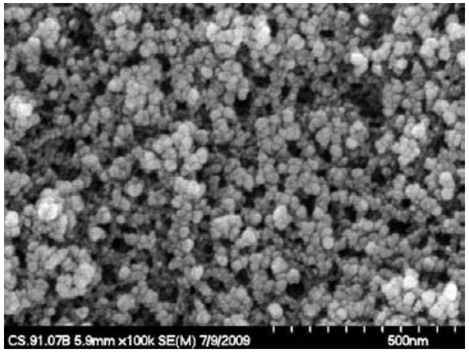
…to high density… and everything in-between

Meador et al, *Chemistry of Materials*, **2007**, *19*, 2247-2260

One pot process streamlines aerogel fabrication







- Eliminating diffusion
  - Shortens process
  - Cross-linking more efficient
  - Aerogels are more uniform
- Properties are the same as multistep when 15 mol % APTES used
- Higher APTES leads to much higher density, lower surface area
  - Diffusion not a factor
  - Amount of polymer cross-linking much higher

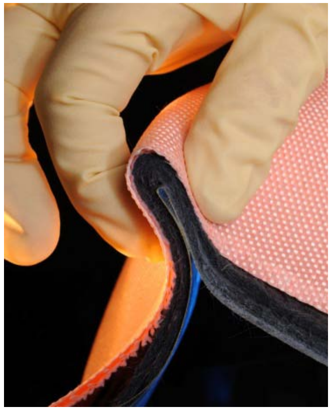
Meador et al, *ACS Applied Materials and Interfaces*, **2010**, 2, 2162-2168

Hypersonic inflatable aerodynamic decelerator concept

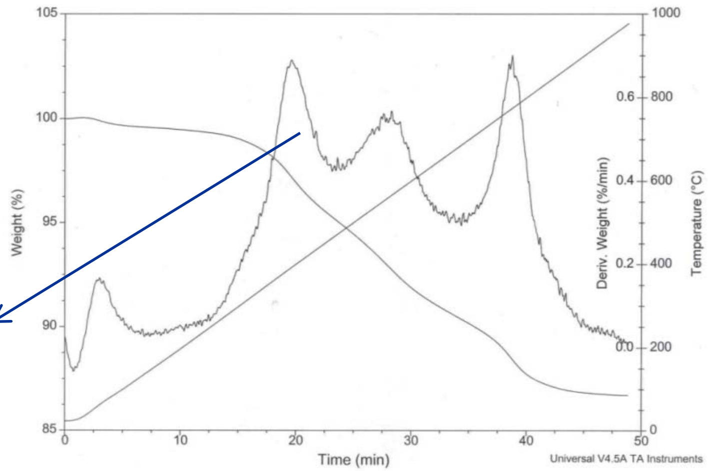
- Hard aeroshells used to land rovers on Mars limit size of payload
- Inflatable structure overcomes this limitation
- Concept shown constructed from a series of stacked inflatable torus tied to each other and to the vehicle with a network of straps
- Flexible thermal protection system on fore body only
- More information about recent successful test launch: http://www.nasa.gov/centers/goddard/news/features/2012/IRVE3.html

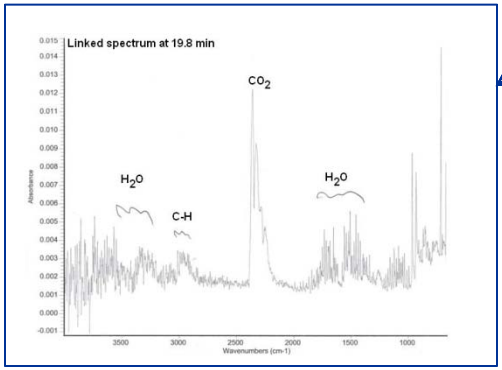


Improved insulation for inflatable re-entry vehicles



- Baseline insulation is Aspen Aerogels Pyrogel 3350
  - Aerogel particles flakes off as sample is handled
  - Organic components outgas at ~375-800 °C
- Needs to be as or more flexible and foldable, less dusty, as or more thermally stable

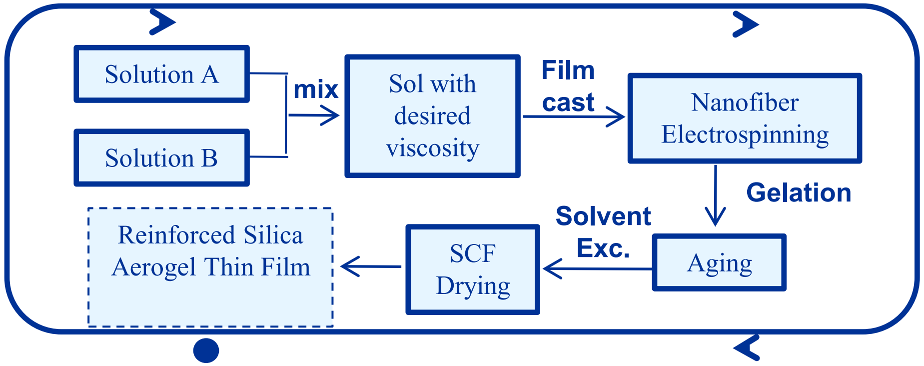




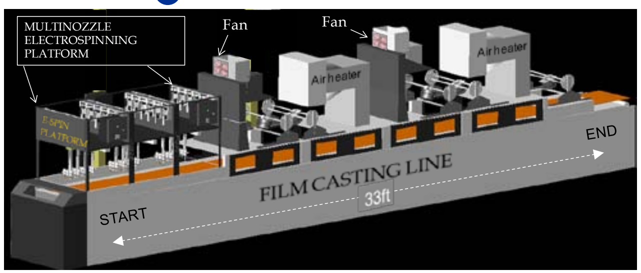
Approaches examined for more flexible aerogel insulation

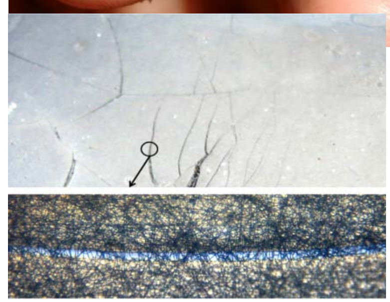
- Thin films
  - Thinner is more flexible than thick
  - Think aluminum foil vs. block of aluminum
- Nanoscale fillers to improve properties
  - Electrospun nanofibers
  - Carbon nanotubes
- Polymer aerogels
  - Silica aerogels and even polymer reinforced silica aerogels are intrinsically stiff
  - Need to examine high temperature stable polyimides

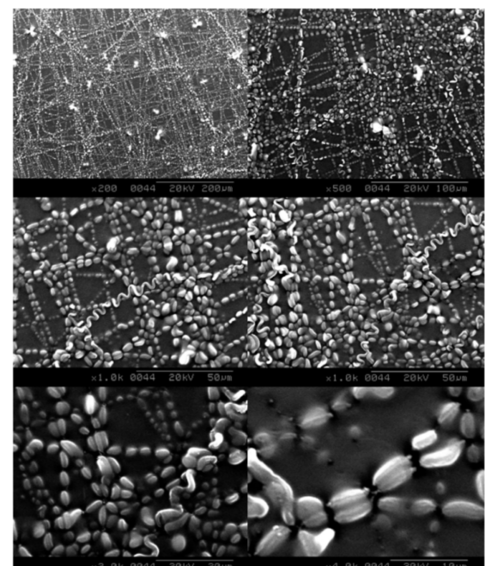
Collaboration with University of Akron—thin film aerogels reinforced with electrospun nanofiber

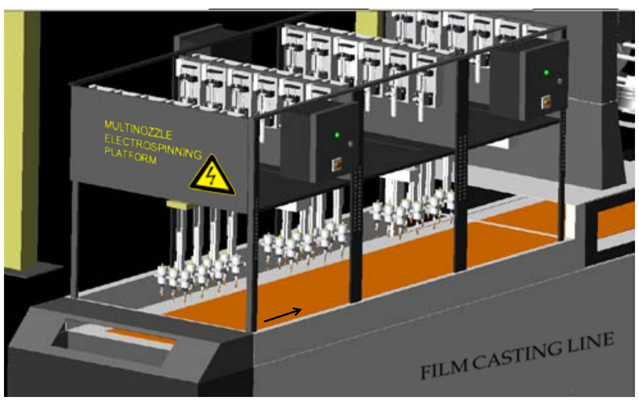


- Sol cast into thin film
- Electrospun fibers of PDMS/PU deposited into film
- Flexible nanofibers bridge cracks/hold structure together



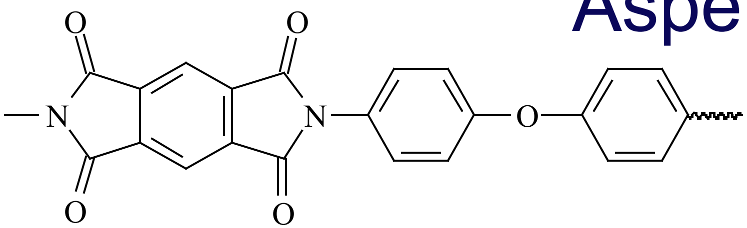






Li et al, *ACS Applied Materials and Interfaces*, **2009**, 1, 2491-2501

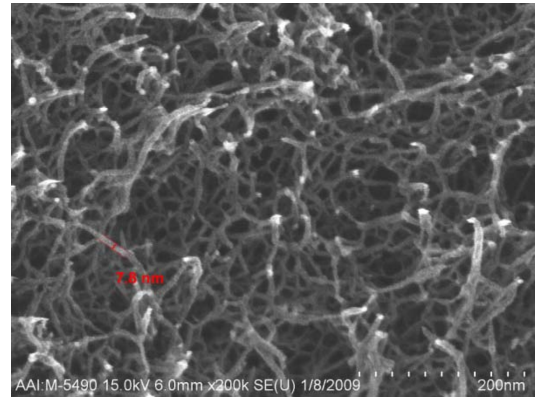
Linear polyimide (PI) aerogels made by Aspen Aerogels



- High MW polyimide gels made from PMDA and ODA
- Supercritical drying produced aerogels
- Onset of decomposition >560 ^{o}C
- As strong or stronger than polymer reinforced silica aerogel
- But much shrinkage on preparation

Wet gel

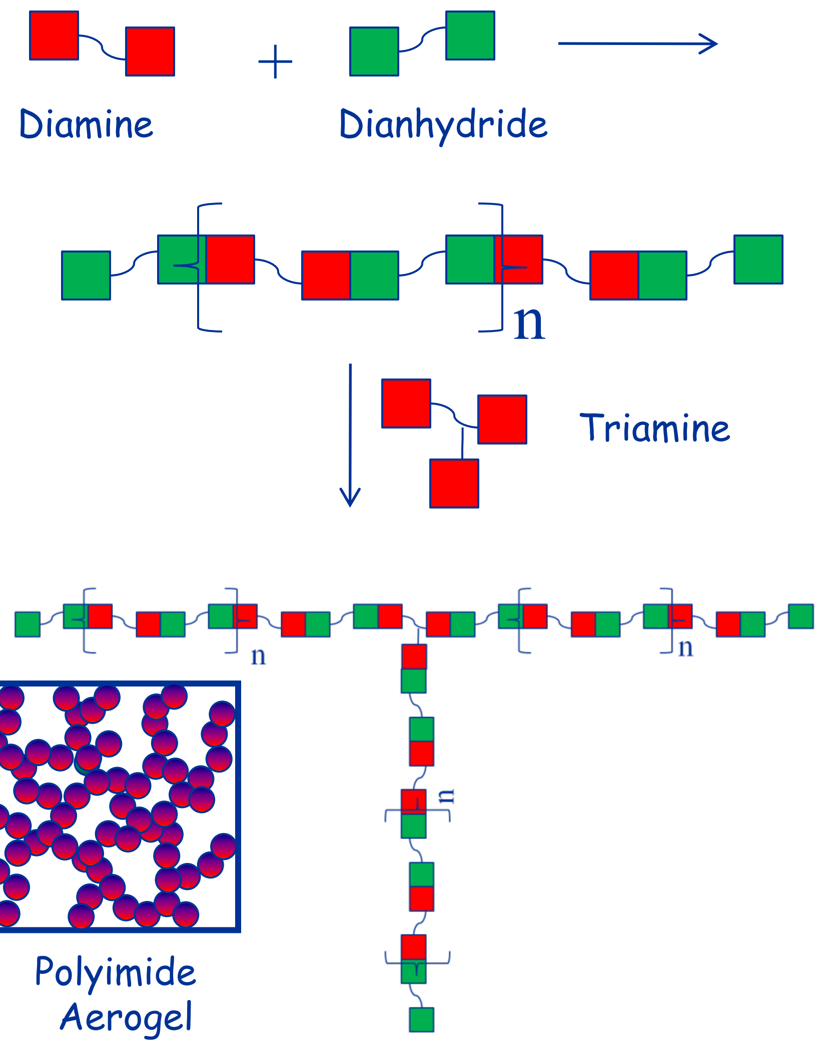
Aerogel

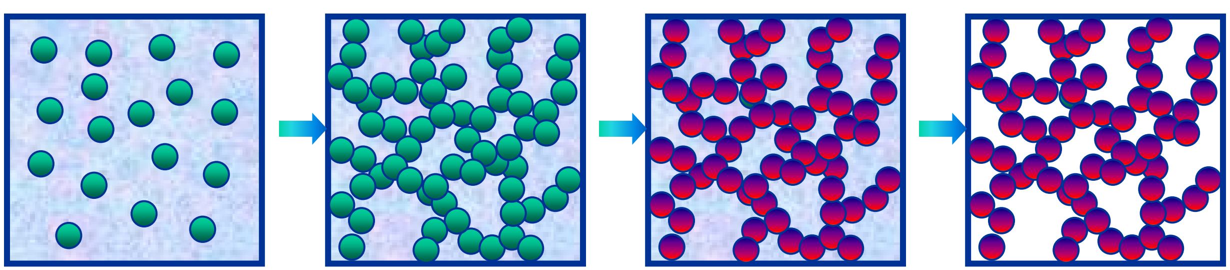


Rhine, Wang and Begag, *US Patent 7,074,880 B2*, July 11, 2006

Cross-linked PI aerogels using branched amines

- Use of triamines, or other multifunctional groups to form network structure
- Gelled polyamic acid network is imidized
- Solvent exchange to acetone then supercritical drying to produce aerogel

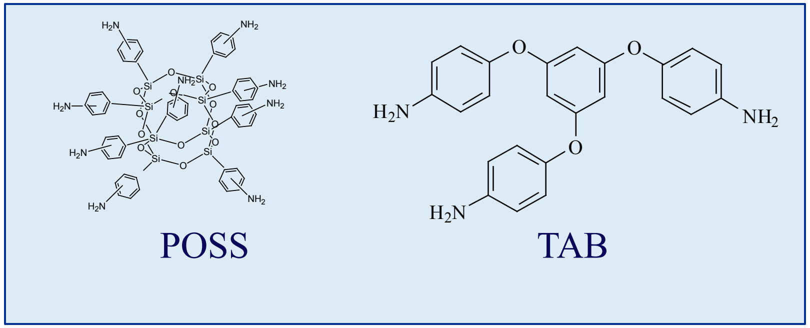




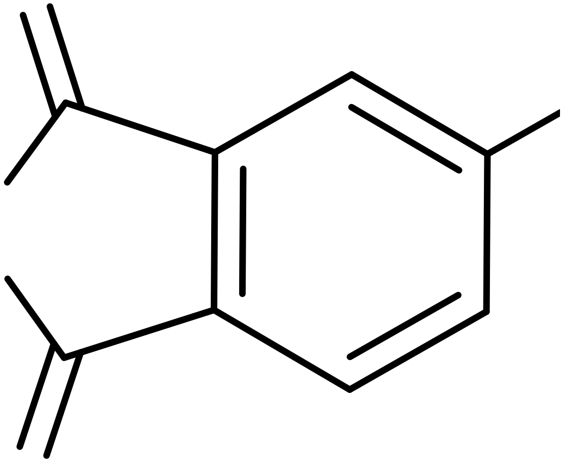
Monomers | Polyamic Acid Gel | Polyimide Gel | Polyimide Aerogel

Meador, US Patent application filed 9-30-2009

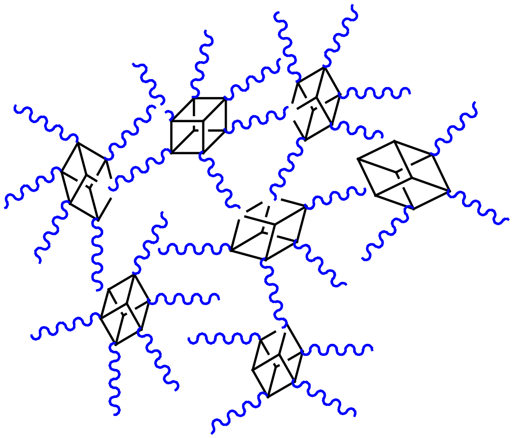
Two approaches to cross-linked PI aerogels developed

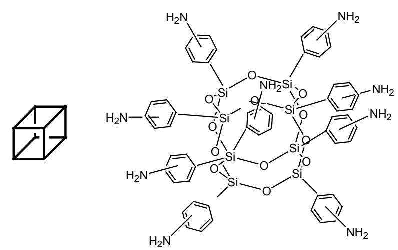


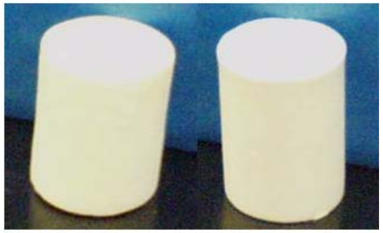
- Network structure formed either through cross-linking with aromatic triamine (TAB) or POSS decorated with eight aminophenyl groups
- Scheme with TAB cross-linking shown



Polyimide 3D network using T8-POSS—first successful formulations



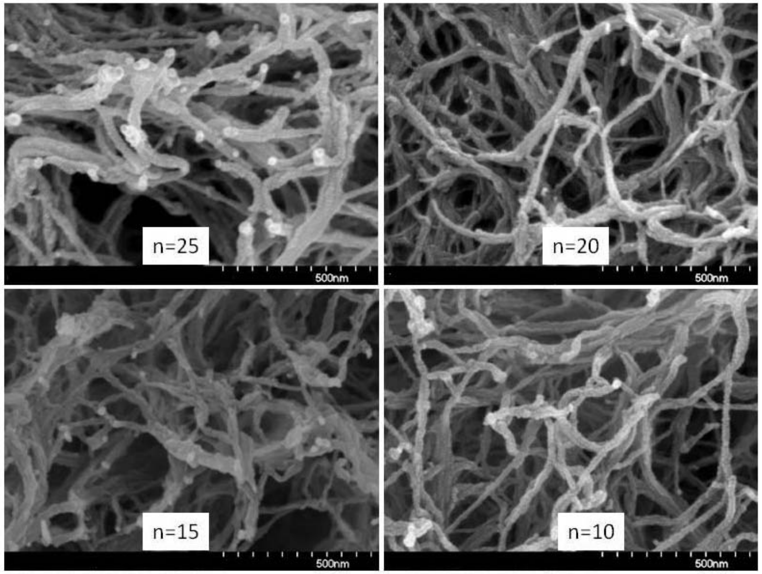




BAX

BPDA BPDA

- PI cross-linked with POSS
- Chemically imidized with pyridine/acetic anhydride
- BPDA-(BAX-BPDA)n; n = 10 to 25
- Low shrinkage (~10 %)
- Density: ~0.1 g/cm^3
- Porosity > 90 %

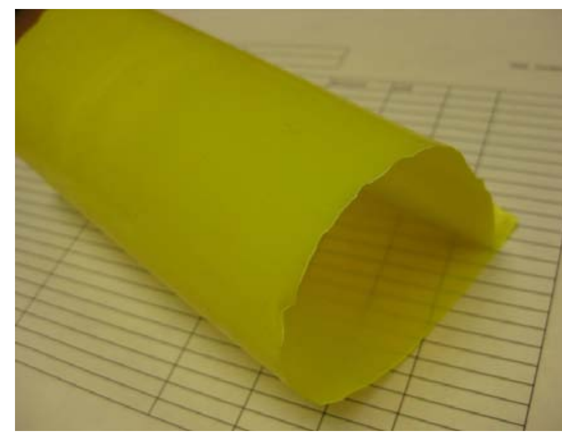


Guo, et al, *ACS Appl. Mater. Interfaces*, **2011**, *3* (2),546-552

Cross-linked polyimide aerogels cast as thin film are flexible

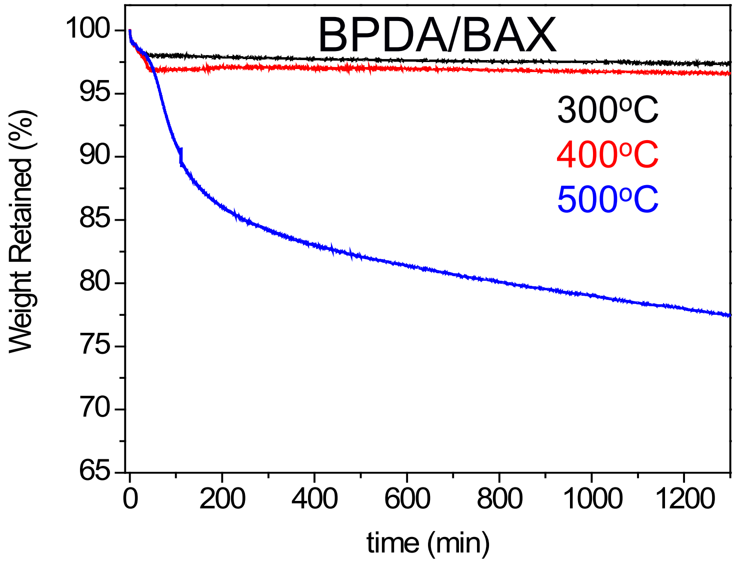
- Collaboration with Miko Cakmak, University of Akron
- Density of film is similar to molded cylinder
- Middle picture is 9” x 13” pan; film is folded multiple times

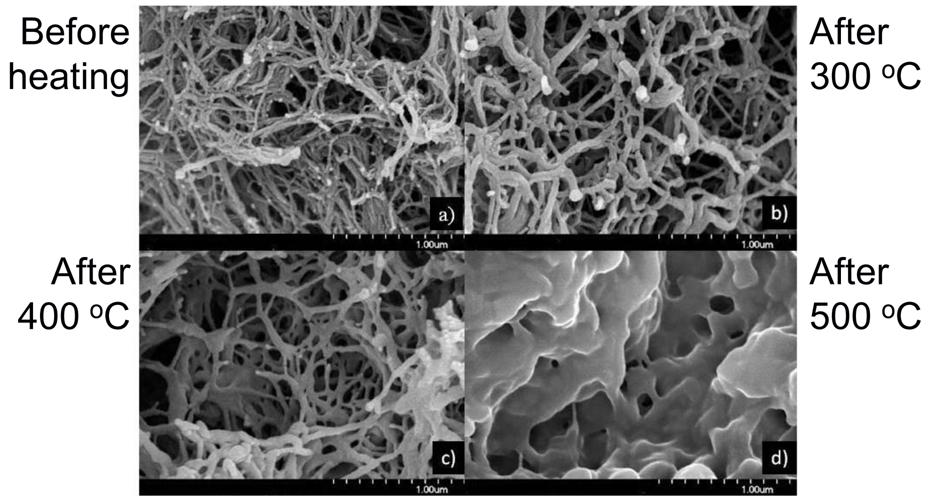
As-cast wet films



Dry aerogel

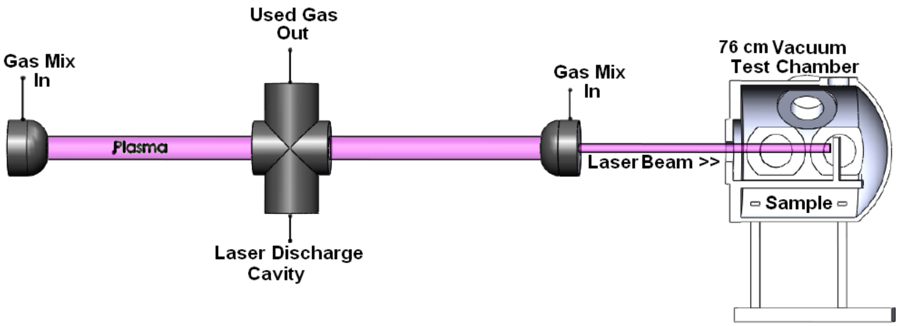
Aging up to 500 ^oC in N_2 for 24 hours

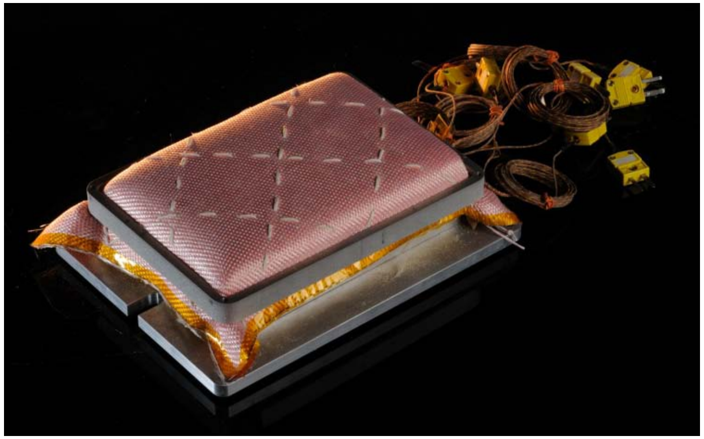




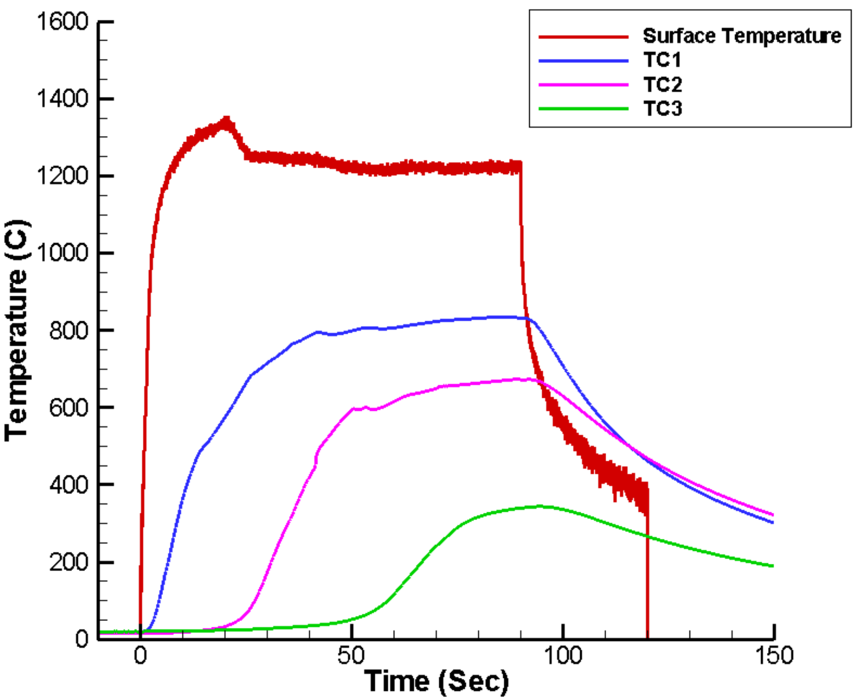
- Very little weight loss, little change in pore structure up to 400 ^oC
- 500 ^oC causes collapse of pore structure

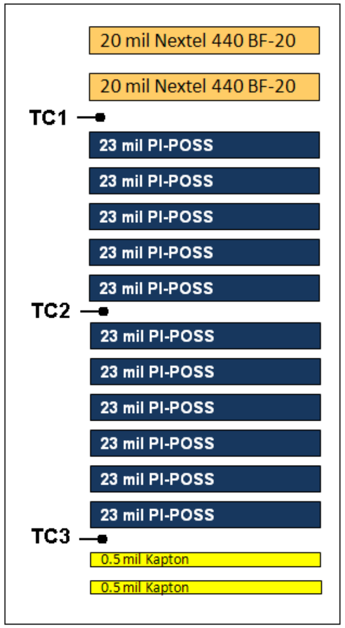
Testing of PI-POSS aerogels under high heat flux





Laser Hardened Materials Experimental Lab Wright Pat





- BPDA/BAX/POSS
- Heat flux 20 W/cm^2, 8 torr N_2
- 90 sec duration
- Bottom layers only darkened, no hole, no cracks

Formulation study of PI-POSS aerogels with different dianhydrides and diamines

PPDA

ODA

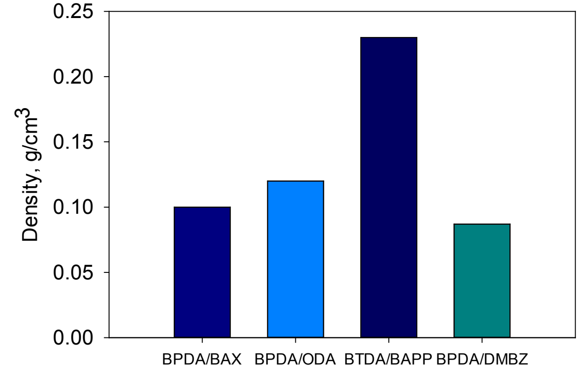
DMBZ

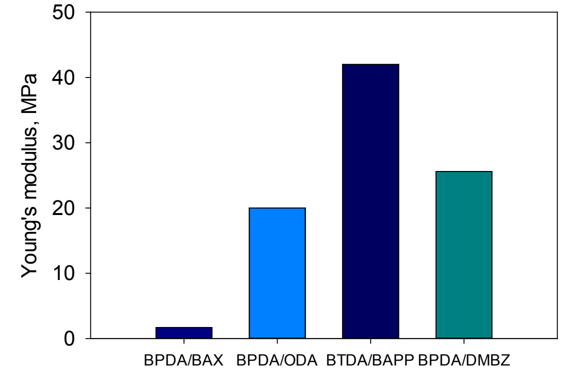
BAX

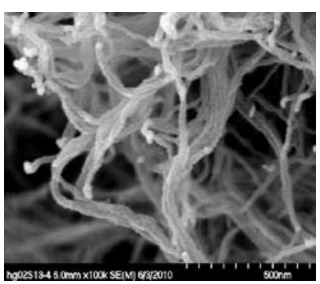
BAPP

BPDA

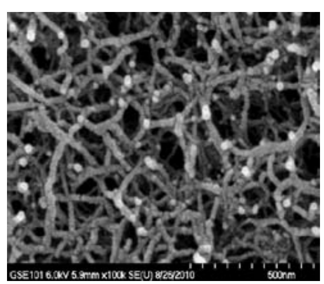
BTDA



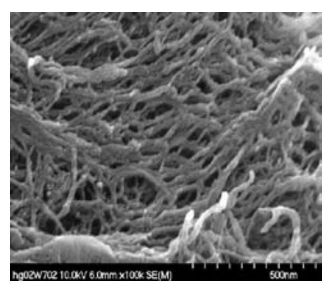




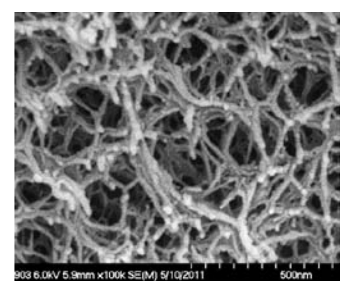
BPDA/BAX



BPDA/ODA



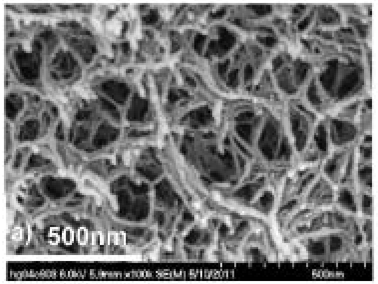
BTDA/BAPP



BPDA/DMBZ

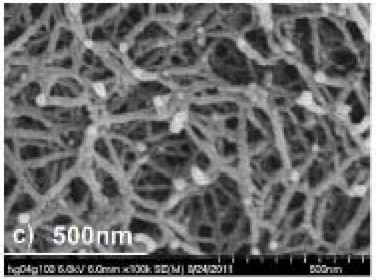
Mixtures of rigid and flexible diamines give better combination of properties

100 % DMBZ



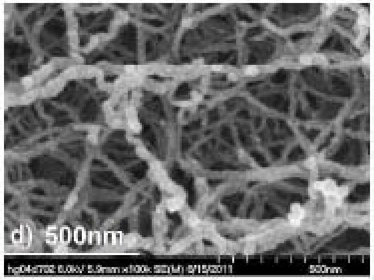
$0.09 g/cm^3$, 94% porous, 498 m^2/g

100 % ODA



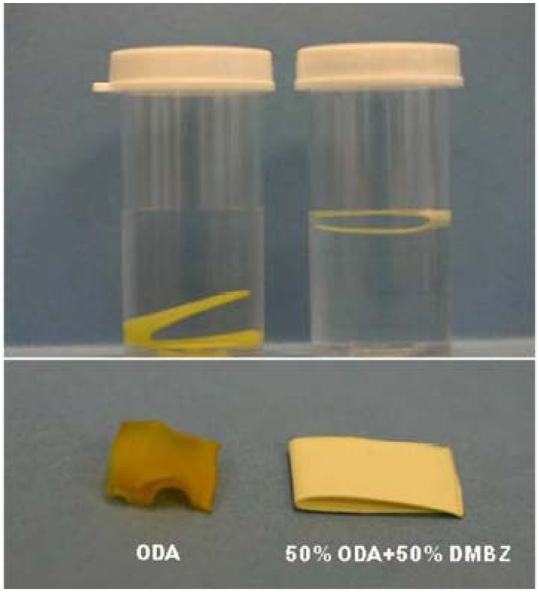
$0.13 g/cm^3$, 91% porous, 295 m^2/g

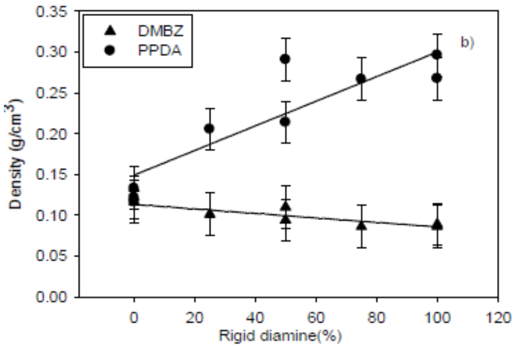
50 % ODA 50% DMBZ

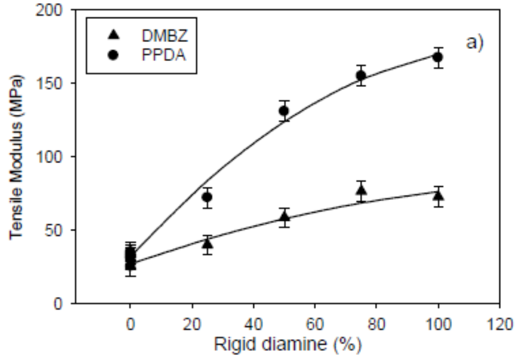


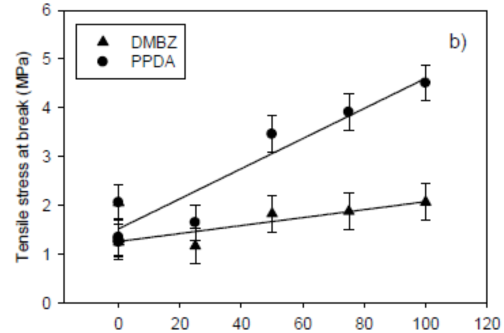
$0.10 g/cm^3$, 93% porous, 392 m^2/g

- 100% DMBZ too stiff
- 100% ODA moisture sensitive
- 50-50 formulation is flexible, strong, moisture resistant



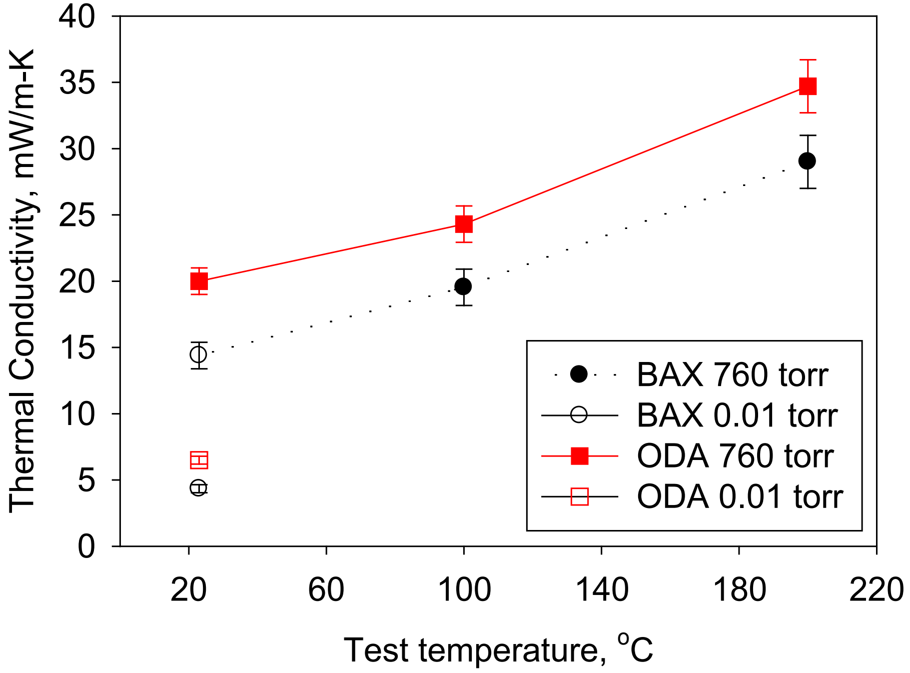






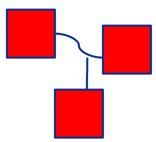
PI-POSS aerogels—thermal conductivity

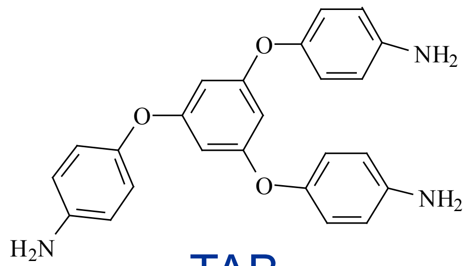
- n = 20 formulation measured at TPRL
- Multiple layers 0.6 mm thick measured
- Comparable to baseline insulation for inflatable decelerator (Pyrogel 3350) in both thermal conductivity and density
- About 5-6 layers equals one layer of Pyrogel 3350
- TC measurements of other formulations are in progress
- Based on density, expectation is that DMBZ formulations will be similar to BAX



PI aerogels cross-linked with 1,3,5-tris(aminophenoxy)benzene,TAB

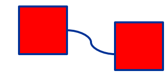
Triamine





TAB

Diamines



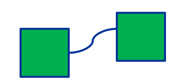
ODA

DMBZ

PPDA

- Varying structure (connecting groups) of diamine and dianhydrides provide means to tailor properties
  - Flexibility
  - Thermal oxidative stability
  - Mechanical properties
  - Thermal conductivity

Dianhydrides



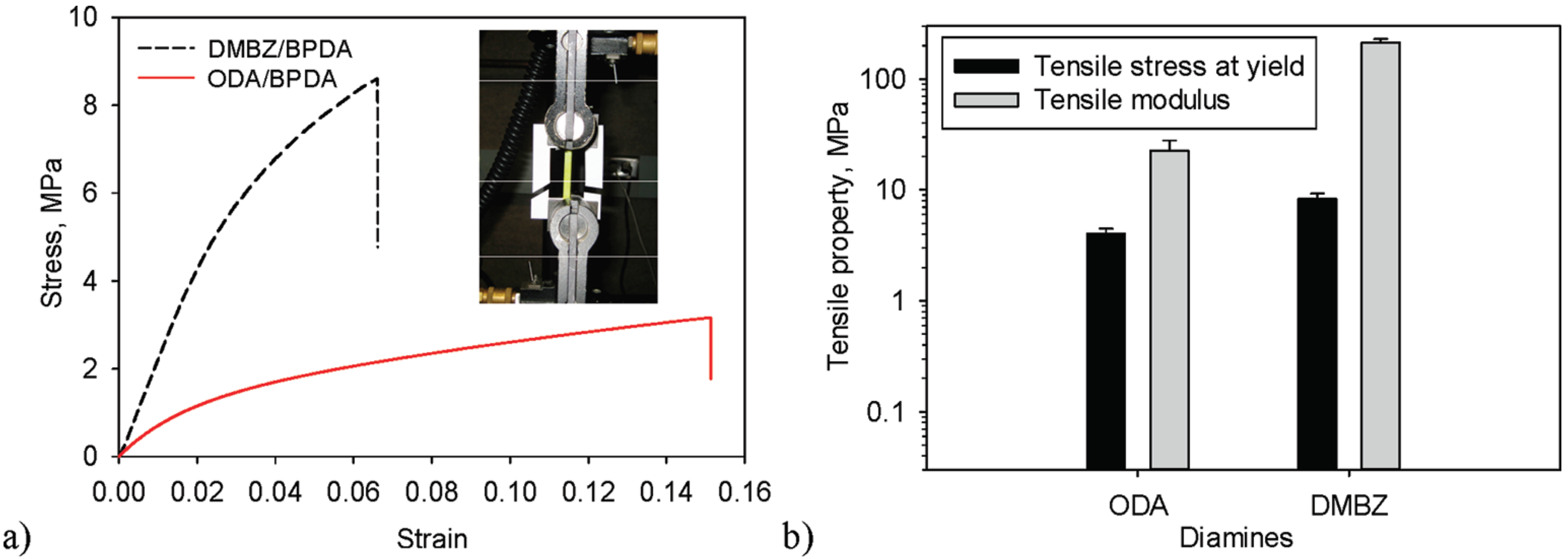
BPDA

BTDA

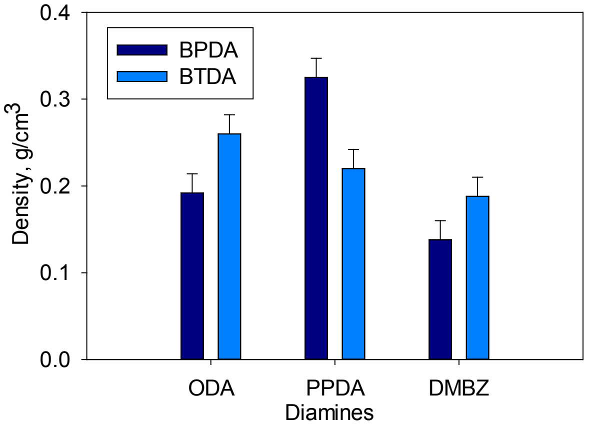
Meador, et al, *ACS Appl. Mater. Interfaces*, **2012**, 4 (3),536-544

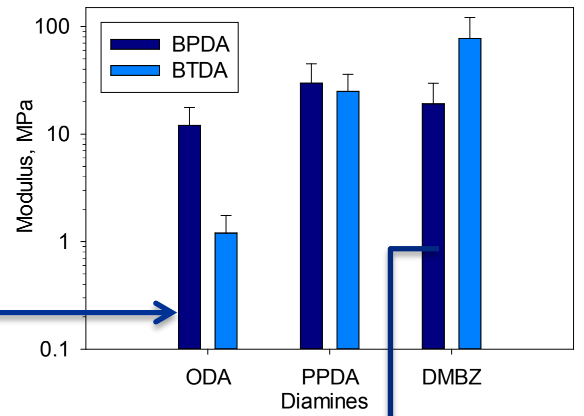
Thin films cast from TAB cross-linked PI aerogels

- TAB/BPDA with either DMBZ or ODA, n = 30
- Higher tensile modulus than POSS films with same backbone chemistry



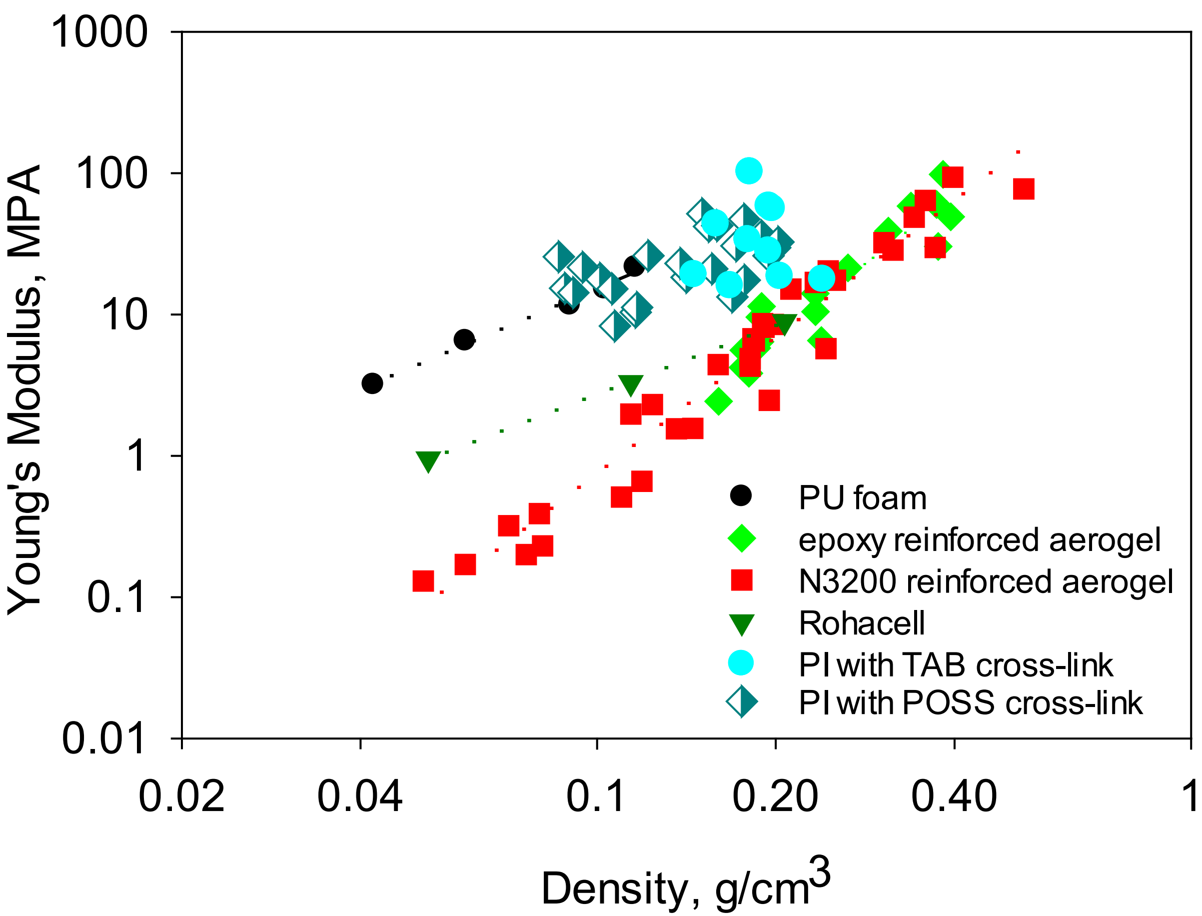
TAB polyimide aerogels strong enough to support weight of a car





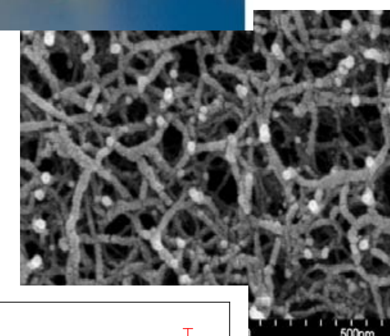
This formulation is actually *stronger* and *lighter* than one shown in picture

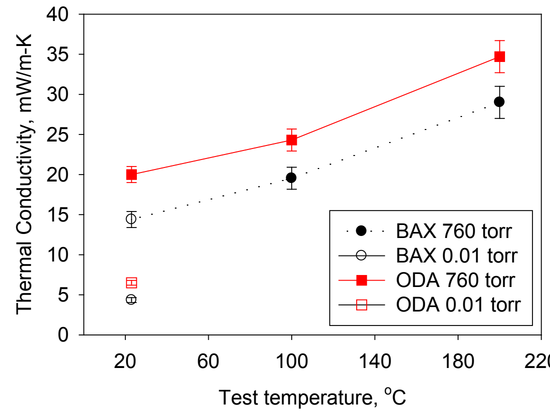
PI aerogels are stronger than polymer reinforced silica aerogels; compare favorably with typical structural foams at the same density



Summary: Polyimide Aerogels

- Two cross-linking approaches evaluated and over twenty different combinations of backbone chemistry
- Formulations identified with
  - Best moisture resistance
  - Best mechanical properties at lowest density
  - Low thermal conductivity
  - Good thermal stability
- Applicable to many terrestrial uses including insulation where silica aerogel blankets are currently used
  - No dusting!
- Future—examining aerogels made from other polymers to improve properties further





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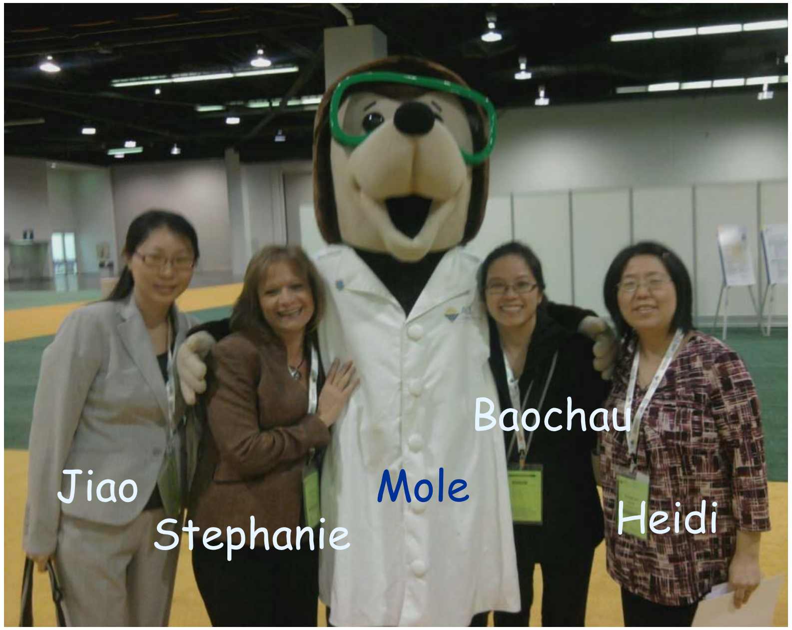

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Thank you!